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Masses for Catalyst Extrusion: Measuring and Optimization of Molding Properties

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Abstract—Methods of measuring the characteristics of molding masses for extrusion are classified. It is suggested that the measurable properties be divided into two groups, one including structural mechanical properties and the other including rheological properties. For estimating the suitability of a molding mass for extrusion of catalysts of preset shape, it is necessary to carry out an integrated analysis of the properties of the mass. The optimum parameters of molding masses have been determined.

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The extrusion molding of plastics has been known since the beginning of the 17th century, when the first ram extruder came into being [1]. In the middle of the 19th century, screw extruders were put into wide use, which ensure a sufficient force in the molding die and allow the molding process to be conducted continuously, which is favorable for a better quality of the resulting pieces. However, in spite of this long history of the process, there is still no consensus as to what properties or combination of properties determines the suitability of a mass for extrusion for obtaining a product with a preset shape.

This problem can be solved by a comprehensive study of the rheological properties of molding masses [2, 3].

Extrusion molding, which is a hydrodynamic process, has its specific features [4, 5]. The most important point here is that the paste should have a certain, sometimes conflicting, combination of rheological properties [3, 6, 7]:

(1) developed plasticity allowing the desired shape to be imparted to the paste;

(2) appropriate yield point ensuring that the "raw" extrudate retains its shape and dimensions at the subsequent processing stages;

(3) fairly strong coagulation structure favorable for maintaining the rheological parameters within the acceptable range just in the molder under high shear stress conditions (in particular, the thixotropic decrease in viscosity should not bring the paste into the minimal-viscosity flow regime).

Molding masses for extrusion are classified as solid-like viscoplastic bodies; that is, depending on the external action, they can behave as a solid or as a liquid [3, 8, 9]. The corresponding methods of estimating the properties of pastes should allow measurement of parameters characterizing a solid, plasticity parameters, and parameters referring to a wide shear stress or shear rate range.

The purposes of this study were the following:

(1) to find the most informative methods of measuring the rheological properties of molding pastes,

(2) to reveal the rheological parameters that can be used as an optimization criterion, and

(3) to optimize the extrusion parameters for producing catalysts and sorbents of preset shape.

Instruments for measuring rheological properties can be classified according to various features. We are interested in classification according to the measuring method [3, 10]. The following methods can be distinguished here:

(1) rotational viscometry (recording the rotation parameters of the operating element of the device in contact with the liquid examined) [11–14];

(2) capillary viscometry (measuring the efflux time for the test material flowing through a capillary with a known cross-sectional area) [5, 11, 12];

(3) measuring the development of tangential shift with time (plane-parallel slit viscometers) [8–11];

(4) penetrometric methods (penetration of an operating element, e.g., cone or die into the test paste) [15, 16];

(5) other methods (oscillating-piston, vibrational, spread, falling- and rising-sphere, and other techniques) [5, 11].

Because of the availability of a wide variety of device types, it is difficult to demarcate the areas of their application. Most devices were designed for express tests, which are convenient for monitoring the rheological properties of materials just during their processing, and these devices are fairly to operate [10, 11, 15, 16]. Below, we will consider only those methods which allow one to estimate parameters having an unambiguous physical meaning.

The devices intended for examining molding masses can also be classified according to the following features [3, 10]:

(1) measurement of elastic and plastic properties under at shear stresses close to the yield point (plastometers) and

(2) measurement of the properties of pastes in the developed flow regime (viscometers).

The parameters measured with type 1 devices will be called structural mechanical parameters, and those measured with type 2 devices will be called rheological parameters.

One of the most important parameters of molding pastes is their water content, According to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, particles in a disperse system may be fixed in two energy minima [9, 17]. The coagulation structure in molding pastes forms upon the fixation of particles in the nearest minimum (short-range coagulation). This state can be identified by measuring plastic strength with Rebinder's conic plastometer [3, 8, 9]. In this technique, plastic strength is estimated from the depth of penetration of the cone into the paste at a known load.

The optimal molding water content is 1–2 wt % lower than the water content corresponding to the formation of short-range coagulation structure and depends considerably on the physicochemical properties of the particle surface, specifically, on its lyophilicity and adsorption capacity and on the specific surface area of the dispersed phase [3, 18, 19].

Measurements using a parallel-plate viscometer yield a set of curves describing the development of strain in the course of time at a constant load [3, 8–10]. The development of strain is quite satisfactorily describable in terms of the Maxwell–Shvedov–Kelvin model, which includes five independent constants:

$$\varepsilon' = \frac{P}{E_1} + \frac{P}{E_2}\left[1 - \exp\left(-\frac{E_2}{\eta_2}t\right)\right] + \frac{P - P_{k1}}{\eta_1}t, \qquad (1)$$

where P is load; ε' is relative strain at P = const; t is the loading time at P = const; the invariant constants E_1 and E_2 are the resilient modulus and elastic modulus, respectively; η_1 and η_2 are the highest and lowest plastic viscosities, respectively; P_{k1} is the ultimate shear stress. From the ratios of these constants, one can calculate some structural mechanical properties, including Volarovich's static plasticity,

$$\mathrm{Pl} = P_{k1}/\eta_1,$$

which characterizes the plastic strain development rate; the proportion of "slow" elasticity in the reversible strain process,

$$\lambda = E_1/(E_1 + E_2)$$

and the relaxation time,

$$\Theta = \eta_1/E,$$

which is the time it takes for elastic strain to decrease by a factor of e = 2.71 and to turn into plastic strain (here, $E = (E_1E_2)/(E_1 + E_2)$ is the equilibrium modulus.

Using model (1), it is possible to calculate reduced strains, namely, resilient (quick elastic) strain ε_{res}, slow elastic strain ε_{el}, and plastic strain ε_{pl}. According to the correlation of these strains, all disperse systems can be divided into six structural mechanical types [20]. The desired correlation of strains in a molding mass depends on the shape to be obtained [3, 6, 7]. For obtaining simple shapes, it is essential that neither the elastic nor plastic strain dominate. In the former case, there would be brittle fracture; in the latter case, the piece would undergo deformation. If it is necessary to produce a complex shape, such as a honeycomb monolith, the range of optimal correlations between different kinds of strain will be substantially narrower.

We demonstrated that the optimum correlation of strains is an insufficient condition for a molding mass to be suitable for extrusion of complex-profile articles, such as honeycomb monoliths [3, 6]. Attempts to extrude some molding pastes with the optimal correlations of strains ran across various undesired phenomena (marked decrease in effective viscosity, difference in paste exit rate between dire channels, etc.), which absolutely ruled out production of honeycomb monoliths. This is due to the fact that measurements using a plastometer are made at shear stresses close to P_{k1}. The actual shear stresses in an extruder are much higher, and this causes the breakup of the coagulation structure and, as a consequence, a large decrease in viscosity. Therefore, in order to more knowingly judge the suitability of a paste for extrusion of articles of preset shape, it is necessary to gain addition information on the rheological properties of the paste.

Information concerning the behavior of a molding paste at higher shear rates can be provided by an analysis of flow curves recorded using a rotational or capillary viscometer. The main advantage of these viscometers is that provided data in absolute physical units [12]. In our study, rheological curves for molding masses were obtained using a Rheotest-2 rotational viscometer with a Searle measurement cell (cone-and-plate technique, shear rates from 2 to 4800 s^{-1}).

The flow curve as such does not allow the molding mass to be unambiguously characterized, but it can be used to calculate the strength of the coagulation structure (Fig. 1). In turn, the necessary strength value depends on the shape to be imparted to the extrudate. The strength of the coagulation structure should be at least 2 MW/m^3 for obtaining simple shapes and at least 20 MW/m^3 for producing honeycomb monoliths [3, 6, 7]. This is due to the fact that the dies for honeycomb monolith extrusion generate a high flow resistance and, accordingly, higher shear stresses develop there.

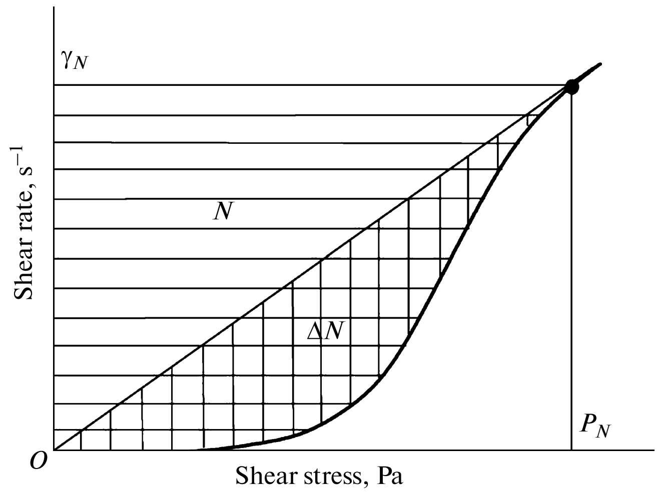


Fig. 1. Complete rheological curve for a molding mass. The $\{P_N, \gamma_N\}$ point indicates the passage of the flow to the Newtonian regime. N is the total power necessary to bring the liquid to the Newtonian flow regime, ΔN is the power required for the total breakup of the coagulation structure.

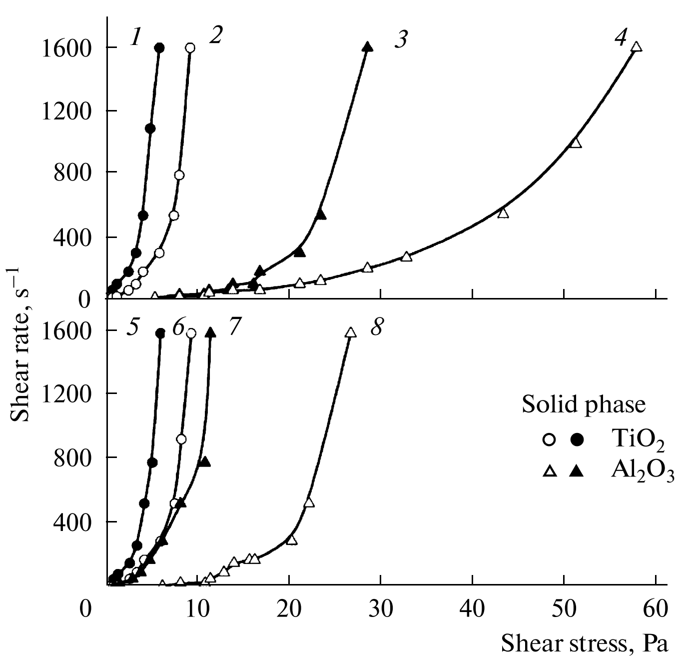


Fig. 2. Rheological curves for molding masses. The relaxation time is (*1*) 46000, (*2*) 1900, (*3*) 2800, (*4*) 700, (*5*) 3100, (*6*) 1050, (*7*) 3000, and (*8*) 500 s.

Of great significance for extrusion are relaxation effects, which can be characterized by a relaxation time. Note that, from the rheological standpoint, there is no fundamental difference between a liquid and a solid and everything depends on the loading value and time [3, 7, 9]. Let us illustrate this point with an example. If the applied load is below the plastic strength of the material and the loading time is shorter than the relaxation time, the strain will disappear entirely after the load is removed. Conversely, if the load exceeds the plastic strength, the plastic strain will persist. If the load is lower than the plastic strength and the loading time is fairly long, part of the strain will disappear, while the part turning into plastic strain will remain.

Investigating the properties of a number of molding masses, we established a correlation between the relaxation time and the strength of the coagulation structure (Fig. 2). As the relaxation time decreases, the strength of the coagulation structure increases. Note that this inference is valid for systems similar in the composition of the solid phase. The strength of the coagulation structure increases mainly owing to the widening of the shear stress range corresponding to the rheological curve segment in which the coagulation structure practically does not break as the suspension flows.

The flow curves of molding masses are fairly well described by the Ostwald–de Waele equations [3, 4]:

$$P = \eta_0 \gamma^n, \quad \eta = \eta_0 \gamma^{n-1}, \qquad (2)$$

where P is the shear stress, γ is the shear rate, η_0 is the consistency constant (Pa s^n), and n is the flow behavior index. The flow behavior index characterizes the deviation of the flow from the Newtonian behavior:

at $n = 1 \mathrm{d}\eta/\mathrm{d}P = 0$ (ideal Newtonian fluid),

at $n < 1$ $\mathrm{d}\eta/\mathrm{d}P < 0$ (thixotropic fluid),

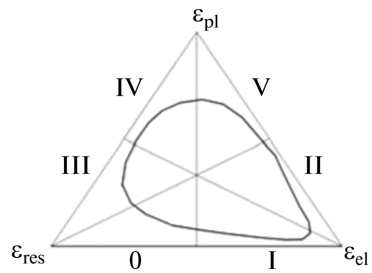
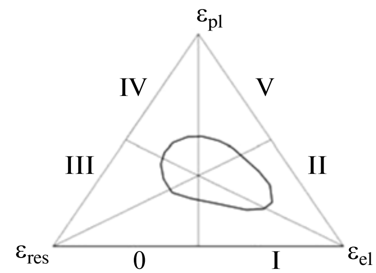
at $n > 1$ $\mathrm{d}\eta/\mathrm{d}P > 0$ (dilatant fluid).

What is the desirable value of the flow behavior index determined from the rheological equation (2)? The radial profile of flow velocity in the die channel is Poiseuille-type. The flow velocity decreases with an increasing distance from the flow axis. When the velocity drop is large, molding is impossible because of the defects generated as a result of the velocity equalization after the exit of the mass from the die channel. The smaller the flow behavior index, the less significant the velocity drop in the central part of the channel and the more easily avoidable the defect formation. In the hypothetical case of $n \to 0$, the plug flow regime takes place.

The table lists the most significant structural mechanical and rheological properties of molding pastes that enable one to more correctly judge their suitability for extrusion of catalysts and sorbents in preset shape. The table also specifies the optimal values of of these parameters for the two limiting cases of obtaining products in the simplest (cylindrical) and most complex (honeycomb) shapes. The numerical values of these parameters were determined by investigating a wide variety of systems: pastes based on aluminum oxide and hydroxide, pastes based on iron compounds, pastes prepared from natural aluminosilicates and various admixtures, etc. [3, 6, 7, 10, 18, 21].

The methods of regulating the properties of molding masses have been considered in detail in our previous works [3, 18, 21].

Optimal parameters of molding masses

Property	Parameter	Parameter	
		simple shape (cylinder, annulus)	complex shape (honeycomb monolith)
Moisture content	moisture content	10–40 wt %	10–30 wt %
Structural mechanical	plastic strength	at least 10 kPa	at least 15 kPa
	correlation of strains		
	relaxation time	300–100000 s	500–2000 s
Rheological	strength of the coagulation structure	at least 2 MW/m^3	at least 20 MW/m^3
	flow behavior index	at most 0.7	at most 0.3

CONCLUSIONS

Depending on the shear stress or shear rate range in which the molding mass is tested, the measurable parameters can be divided into structural mechanical and rheological ones.

Use of a single method does not allow one to draw an unambiguous conclusion as to the suitability of the molding mass for extrusion. An integrated study of the mass is necessary for this purpose.

The molding mass parameters exerting the strongest effect on extrusion have been determined, and their optimal values are presented in the table.

REFERENCES

1. Doll, G., Handle, F., and Spiessberger, F., *Extrusion in Ceramics,* Berlin: Springer, 2007, p. 259.
2. Ovchinnikov, P.F., *Vibroreologiya* (Vibrorheology), Kiev: Naukova Dumka, 1983.
3. Prokof'ev, V. and Gordina, N., *Ekstruziya katalizatorov i sorbentov: Fiziko-khimicheskaya mekhanika i reologiya* (Extrusion of Catalysts and Sorbents: Physicochemical Mechanics and Rheology), Saarbrücken, Germany: Lambert Academic, 2011.
4. Malkin, A.Ya. and Isayev, A.I., *Rheology: Concepts, Methods and Applications*, Toronto: ChemTec, 2006.
5. Gleissle, W. and Graczyk, J., *Extrusion in Ceramics*, Berlin: Springer, 2007, p. 161.
6. Prokof'ev, V.Yu., Il'in, A.P., Shirokov, Yu.G., and Yurchenko, E.N., *Zh. Prikl. Khim.*, 1995, vol. 68, no. 4, p. 613.
7. Prokof'ev, V.Yu., *Steklo Keram.*, 2011, no. 1, p. 11.
8. Rebinder, P.A., *Izbrannye trudy. Poverkhnostnye yavleniya v dispersnykh sistemakh. Fiziko-khimicheskaya mekhanika* (Selected Works: Surface Phenomena in Disperse Systems and Physicochemical Mechanics), Moscow: Khimiya, 1979.
9. Kruglitskii, N.N., *Osnovy fiziko-khimicheskoi mekhaniki* (Fundamentals of Physicochemical Mechanics), Kiev: Vishcha Shkola, 1975, part 1.
10. Prokof'ev, V.Yu., *Steklo Keram.*, 2010, no. 4, p. 22.
11. Alfani, R. and Guerrini, G.L., *Mater. Struct.*, 2005, vol. 38, no. 2, p. 239.
12. Schramm, G., *A Practical Approach to Rheology and Rheometry*, Karlsruhe: Gebrueder Haake, 1994.
13. Pivinskii, Yu.E., *Ogneupory*, 1995, no. 12, p. 11.
14. Roussel, N., *Mater. Struct.*, 2007, vol. 40, no. 10, p. 1001.
15. Fadeeva, V.S., *Formuemost' plastichnykh dispersnykh mass* (Moldability of Dispersed Plastic Masses), Moscow: Gosstroiizdat, 1961.
16. Balkevich, V.L., Mosin, Yu.M., and Firsova, M.N., *Steklo Keram.*, 1980, no. 4, p. 16.
17. Kendall, K., *Molecular Adhesion and Its Applications: The Sticky Universe*, New York: Kluwer, 2004.
18. Prokof'ev, V.Yu. and Il'in, A.P., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2001, vol. 44, no 2, p. 72.
19. Baran, B., Ertürk, T., Sarikay, Y., and Alemdaroğlu, T., *Appl. Clay Sci.*, 2001, vol. 20, nos. 1–2, p. 53.
20. Nichiporenko, S.P., *Osnovnye voprosy teorii obrabotki i formovaniya keramicheskikh mass* (Topics in the Theory of Processing and Moldability of Ceramic Batches), Kiev: Akad. Nauk USSR, 1960.
21. Il'in, A.P. and Prokof'ev, V.Yu., *Katal. Prom–sti.*, 2002, no. 6, p. 45.